New Photochemical Synthesis of Transparent Conducting Polydithieno[3,4-*b*; 3′,4′-*d*]Thiophene

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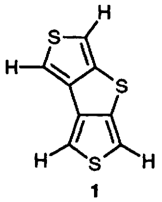
The preparation of conducting polydithieno[3,4-b; 3′,4′-d]thiophene *via* photochemical polymerisation leads to a thin film with electrochromic properties in the visible region.

Polydithieno[3,4-*b*; 3′,4′-*d*]thiophene (PDTT) has been recently synthesised[1] *via* electrochemical polymerisation; this conjugated polymer exhibits low energy gap ($E_g = 1.1$ eV), good conductivity and stability and is transparent in the visible spectral region.[2] In the field of conjugated materials a low E_g is a desirable feature for intrinsically conducting polymers and if they display a suitable spectral window of transparency they may be useful in electrochromic devices.

We now report a new and easy synthesis to prepare PDTT which gives the polymer both in powder and in thin film for applications in optical devices.

The dithieno[3,4-*b*; 3′,4′-*d*]thiophene (DTT) **1** monomer was prepared following literature methods.[3] Photopolymerization of DTT was carried out in a RPR-100 Rayonet photoreactor equipped with 16 low pressure Hg lamps irradiating at 254 nm. In a typical experiment 0.046 g (0.235 mmol) of DTT were dissolved in 2.8 ml of acetonitrile containing 0.02 ml of CCl_4 and 0.009 g (0.0279 mmol) of tetrabutylammonium bromide. The solution was carefully degassed with bubbling nitrogen for 20 min and successively irradiated for 10 h in a quartz vessel. At the end of the irradiation a black precipitate was formed as well as a dark film on the walls of the vessel. The film thickness and its optical density were found to be a function of the irradiation time. The reaction mixture was filtered and the black precipitate was carefully washed twice with methanol. This solution was evacuated and a NMR spectrum was carried out in deuterioacetone of the residue, which principally constituted the oligomers. Two doublets centred at δ 7.35 and 7.80 bring us to tentatively assign the polymerisation to the positions 2 and 5 in one thiophene ring. The observed downfield shift with respect to the reported monomer values[3] may be explained by the enhanced conjugation in the oligomers. This is also in line with the behaviour of the thiophene system for this kind of reaction.[4]



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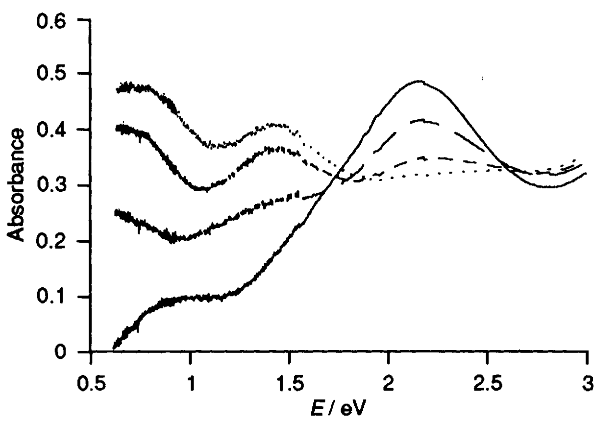

Fig. 1 Electron absorption spectra of PDTT film recorded *in situ* during the electrochemical doping. (–) neutral, (- -) light doped, (— — —) doped, (- - - -) full doped.

The powder in pressed pellets shows a conductivity of 5×10^{-2} S cm^{-1} measured with the two probe technique. Both powder and films have been characterised as PDTT by elemental analysis,† FTIR and UV–VIS–NIR spectroscopy and by comparison with the electrochemically prepared polymer.

PDTT can be photopolymerised in thin films on different supports, such as semiconducting indium–tin oxide (ITO) plated glass. We have studied the electrochemical doping–dedoping process of a PDTT thin film following the evolution of electronic absorption spectra. The '*in situ*' optoelectrochemical experiment has been achieved in a quartz cuvette, containing a tetrabutylammonium bromide solution in acetonitrile and PDTT grown on ITO glass as electrode, by applying a constant current of 0.1 mA cm^{-2} for various periods of times. In Fig. 1 the UV–VIS–NIR spectra during a doping–dedoping process are reported: the neutral polymer shows a strong absorption in the visible region (maximum at 2.14 eV) due to the π–π^* transition and has an energy gap (defined as the onset of the optical transition) $E_g = 1.1$ eV. During the doping the π–π^* absorption decreases while two broad bands due to the charge carriers appear in the near infrared. PDTT displays a strong electrochromic effect in the visible region between the neutral (insulating) polymer, which is dark blue, and the doped (conducting), which is quite transparent. The electronic spectrum evidences this effect: the absorbance of the neutral PDTT at 580 nm decreases by 44% after doping.

X-ray diffraction patterns were recorded from powder samples enclosed in glass capillaries using Ni filtered Cu-Kα radiation and an evacuated Debye camera. Irrespective of the method of polymerisation of the PDTT samples, their spectra show a single very broad peak corresponding to an interplanar spacing of 3.5 Å. This value compares well with the one reported in previous studies[5] and is similar to the stacking spacing perpendicular to the molecular plane determined for some oligothiophenes.[6,7] The spectra suggest that the molecules, which probably have a flat ribbonlike structure, achieve some ordering only in the direction perpendicular to the molecular plane. Since the mentioned reflection is somewhat sharper for the photochemically polymerised PDTT it appears that a higher stacking regularity is achieved in that case. Additional sharp diffraction lines may appear in the diffraction patterns, especially in the case of electrochemically polymerised PDTT, due to salt crystallites dispersed in the polymer as a consequence of the polymerisation procedure. In photochemically polymerised PDTT these impurities are very often hardly detectable by X-ray diffraction.

The DTT photopolymerization can produce both polymer powder and thin films on different substrates. The PDTT films are semitransparent and have apparently good optical qualities for applications in electrochromic devices.

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† The elemental analysis of the photochemical prepared PDTT is consistent with the formula $(C_8H_2S_3Br_{0.12})_n$ (Found: C, 47.25; H, 1.02; Br 4.68; S, 46.96. Calcd.: 47.15; H, 0.98; Br, 4.72; S, 47.15).

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